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RESULTS OF ANALYSIS OF URANIUM TAILINGS SAMPLES FOR DETERMINATION OF RECOMMENDED VALUES FOR REFERENCE URANIUM TAILINGS

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1. INTRODUCTION

At present one of the most reliable methods for routinely determining analytical precision and accuracy in commercial geochemical and assay laboratories is by the repeated analysis of reference standards established by different government agencies. Although reference standards are now available for a wide range of sample matrices (e.g. soil, rock, vegetation) frequent introduction of new standards is essential to cover all possible sample media types which may be encountered during routine analysis. Reference standards must be homogeneous to avoid variations introduced when subsamples are taken for analysis. Moreover, the recommended values should as far as possible be "total" element abundances, matrix effects within the standards must be identified and most important the precision and accuracy of the recommended values established by different analytical laboratories must be documented. This report describes the analysis of four uranium tailings samples (UTS 1-4) for Ni, Fe, Ti, Al, Ca, Th, U, As, S and SO_4 with the objective of establishing recommended values so that the reference standards may be confidently employed in the control of precision and accuracy in commercial analytical laboratories.

2. ANALYTICAL TECHNIQUES

2.1 DETERMINATION OF Al, Ca, Ti, Fe, AND Th, BY INDUCTIVELY COUPLED ARGON PLASMA EMISSION SPECTROSCOPY (I.C.A.P.)

The following procedure was used for analysis of the samples:

a) A 0.25 g portion of sample material was mixed with 2 mls conc. HNO_3 and 2 mls conc. $HClO_4$.

b) The mixture was refluxed for 2 hours in a teflon beaker covered with a watch glass.

c) 8 mls of conc. HF were added to the beaker and the contents evaporated to dryness.

d) The residue was dissolved in 1 ml conc. HCl, diluted to 10 mls with 0.5 M HCl.

e) The solution was cooled and diluted to 25 mls in a volumetric flask.

f) A portion of the solution was aspirated into the nebulizer of a calibrated ARL model QA-137 inductively coupled argon plasma emission spectrophotometer and element abundances determined.

2.2 DETERMINATION OF Al, Ca, Ti, Fe, and Ni, BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

The same technique was used for sample digestion as that described for I.C.A.P. determination. The solution was aspirated into a Varian model A.A.5 spectrophotometer operated in the absorption mode. Iron was determined by direct

aspiration. Nickel was also determined by direct aspiration, but with background correction applied. Aluminum and titanium were measured by spiking the final solution with potassium (final concentration 2,000 ppm K). Calcium was measured after spiking the solution with a 1% lanthanum chloride solution.

2.3 TOTAL SULPHUR

a) A 0.5 g sample was mixed a Cu-Fe accelerator in a fire clay crucible.

b) The sample was combusted inductively in an oxygen stream in a Leco total carbon-total sulphur analyzer.

c) The SO_2 liberated was titrated against standard KIO_3 solution using a starch-iodide indicator and the sulphur content subsequently determined.

2.4 SULPHATE SULPHUR

Sulphate sulphur was determined by measuring the content of sulphide sulphur in the sample using a hydriodic acid digestion and estimating the sulphate sulphur content by difference between total sulphur and sulphide sulphur. Sulphide sulphur was determined by the following technique:

a) A 5 g portion of the sample was mixed with 2 mls of HI solution (equal volumes of conc. HCl and an aqueous solution containing 50 g of KI in 100 mls) and the H_2S thus evolved was purged with N_2 for 1 hr into a solution of cadmium acetate (2 g in 100 mls H_2O).

b) After all the H_2S had been evolved a standard iodine solution was added to the cadmium acetate and sufficient acetic acid to give a final acid concentration of roughly 0.5 M.

c) The excess iodine was titrated with sodium thiosulphate solution to determine the concentration of sulphur present.

d) Sulphate was estimated by the difference of between total (Leco) sulphur and sulphide sulphur.

2.5 DETERMINATION OF ARSENIC

a) A 0.25 g portion of the sample was fused with $KHSO_4$ and leached with 10 mls of 6 M HCl for 3 hours.

b) Arsenic was measured after hydride generation employing $NaBH_4$ reduction on a Varian A.A.5 atomic absorption spectrophotometer equipped with a heated quartz tube assembly.

2.6 DETERMINATION OF URANIUM BY FLUORIMETRY

Uranium was measured in an aliquot of the same solution used for atomic absorption spectrophotometry and I.C.A.P.

a) 2 mls of the solution were added to 8 mls of aluminum nitrate (saturated solution).

b) The uranium was extracted into 3 mls of ethyl acetate.

c) A 0.2 ml aliquot of the organic extract was pipetted onto a sodium lithium fluoride tablet and fused at high temperature.

d) The fluorescence of the tablets was measured using a calibrated Jarrell Ash fluorimeter and the uranium abundance calculated.

2.7 DETERMINATION OF URANIUM BY DELAYED NEUTRON COUNTING

A 1 g portion of the sample was irradiated for a short time in a small nuclear reactor and the neutrons emitted by fission products, corrected for different isotope abundances, counted to establish the uranium 235 abundance.

2.8 DETERMINATION OF THORIUM BY NEUTRON ACTIVATION

A 0.5 g portion of sample was irradiated in a Slowpoke reactor for approximately 5 days and the thorium content established by counting. Detection levels for elements determined by the different techniques are tabulated in Table 1.

TABLE 1

Detection Levels for Elements Determined by the Different Techniques.

Element	I.C.A.P.	A.A.	FLUO.	NA	DNC	LECO	SULPHIDE
Al_2O_3%	0.01	.01					
CaO%	0.01	.01					
TiO_2%	0.001	.01					
Fe_2O_3%	0.01	.01					
Th ppm	5			1			
U ppm			0.5		0.1		
Ni ppm	1	5					
S%						.01	.01
SO_4%							.01
As ppm		0.1					

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FILE: T3-0002
DATE: 31/03/83
MATRIX: HF

DEPT. OF ENERGY MINES & RESOURCES.CANMET H. F. SIEGER

WO NO: 83-0002

SAMPLE ID	AL2O3-ICAP%	AL2O3-AA %	CAO-ICAP%	CAO-AA %	TIO2-ICAP%	TIO2-AA %	FE2O3-ICAP%	FE2O3-AA %
UTS-1	12.0	11.9	7.41	7.31	.892	.97	6.87	6.90
UTS-1	12.0	11.1	7.39	7.45	.926	1.05	6.79	6.78
UTS-1	11.9	11.1	7.37	7.45	.902	.97	6.90	6.78
UTS-1	12.0	11.2	7.31	7.45	.908	.97	7.04	6.90
UTS-1	12.2	11.3	7.24	7.45	.936	.97	6.90	6.90
UTS-2	5.29	4.92	.603	.66	.231	.23	4.50	4.34
UTS-2	5.19	4.84	.581	.66	.238	.23	4.49	4.47
UTS-2	5.14	4.78	.581	.66	.226	.23	4.54	4.47
UTS-2	5.23	4.86	.589	.66	.205	.23	4.55	4.47
UTS-2	5.22	4.86	.578	.66	.217	.23	4.55	4.47
UTS-3	11.2	10.5	5.49	5.59	.326	.37	4.33	4.74
UTS-3	11.4	10.6	5.58	5.59	.341	.37	4.81	4.74
UTS-3	11.3	10.5	5.33	5.59	.340	.37	4.68	4.67
UTS-3	11.3	10.5	5.58	5.59	.343	.37	4.67	4.74
UTS-3	11.4	10.6	5.55	5.59	.352	.37	4.65	4.74
UTS-4	12.0	11.2	2.41	2.53	.354	.37	3.66	3.84
UTS-4	12.0	11.2	2.51	2.53	.354	.37	3.69	3.84
UTS-4	12.0	11.2	2.45	2.53	.325	.37	3.60	3.84
UTS-4	11.8	11.0	2.45	2.53	.307	.37	3.60	3.71
UTS-4	12.0	11.2	2.47	2.53	.357	.37	3.66	3.84

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SAMPLE ID	TH-ICAP PPM	TH-NA PPM	U-FLUO PPM	U-DNC PPM	NI-ICAP PPM	NI-AA PPM	S %	SO4= %	AS PPM
UTS-1	136	130	65.0	51.3	44.7	45	.95	.94	4.4
UTS-1	142	140	60.0	53.7	39.1	45	.96	.96	4.4
UTS-1	139	130	65.0	49.5	44.5	40	.93	.92	4.8
UTS-1	136	140	60.0	51.2	45.0	40	.93	.92	4.8
UTS-1	141	130	55.0	48.8	44.7	45	.96	.95	4.0
UTS-2	179	170	60.0	53.7	26.2	25	2.98	2.91	20.4
UTS-2	179	170	50.0	53.8	25.8	25	2.98	2.95	18.8
UTS-2	179	160	60.0	53.3	25.4	25	3.00	2.94	20.8
UTS-2	187	160	60.0	54.5	25.8	25	2.93	2.89	19.6
UTS-2	173	180	60.0	54.0	25.5	25	3.03	3.00	20.4
UTS-3	25.3	10	500	531	29.3	25	.22	.21	3.6
UTS-3	26.7	9	500	519	30.9	25	.21	.21	4.0
UTS-3	22.7	9	500	520	29.1	25	.21	.21	3.6
UTS-3	25.2	9	500	528	29.6	25	.20	.20	3.6
UTS-3	25.2	9	500	519	31.4	25	.20	.20	4.0
UTS-4	38.2	15	1050	991	121	85	1.69	1.68	36.8
UTS-4	38.1	14	1020	996	121	85	1.68	1.67	36.8
UTS-4	31.2	14	1050	985	122	85	1.68	1.67	36.8
UTS-4	31.2	14	1050	998	121	85	1.70	1.69	33.6
UTS-4	38.2	14	1050	999	122	85	1.72	1.71	34.4

3. RESULTS

The data for Al, Ca, Ti, Fe, Th, U, Ni, S, SO_4 and As, generated by repeated analyses of the tailing samples, are given in Table 2. Mean values and percent relative standard deviations based on 5 determinations of elements in each sample are given in Table 3. In general, there is close similarity between Al, Ca, Ti, Fe, and Ni values established by I.C.A.P. and A.A. methods and the RSD values are below 7%. Uranium concentrations measured by the fluorimetric technique are slightly higher than those obtained by delayed neutron counting. In addition, the RSD values are higher for the fluorimetric technique and this could reflect the lower sensitivity of the method. Thorium values obtained by I.C.A.P. are higher than those obtained by neutron activation which could reflect the influence of the high uranium levels in samples UTS 3 and 4 on the I.C.A.P. technique. In all the samples the sulphate content established by difference between sulphide and total sulphur is more than 90% of the total sulphur abundance in the samples.

Mean, RSD and recommended values for the CANMET standards SY-2, SY-3 and MRG-1, used to establish quality control during analysis of the four tailings samples are given in Tables 4, 5 and 6. These data show that analytical precision for all the techniques employed is better than 4% and that values obtained during analysis are similar to the recommended values for the CANMET standards.

TABLE 3

Mean and Percent Relative Standard Deviation of
Five Measurements for Samples UTS1-4

Standard	Al_2O_3 (ICAP) Mean (%)	RSD	Al_2O_3 (AA) Mean (%)	RSD	CaO (ICAP) Mean (%)	RSD	CaO (AA) Mean (%)	RSD
UTS-1	12	0.92	11.3	2.96	7.34	0.94	7.42	0.84
-2	5.2	1.06	4.9	1.04	0.59	1.73	0.66	0
-3	11.3	0.74	10.5	0.52	5.51	1.91	5.59	0
-4	12	0.75	11.2	0.80	2.46	1.48	2.53	0

Standard	TiO_2 (ICAP) Mean (%)	RSD	TiO_2 (AA) Mean (%)	RSD	Fe_2O_3 (ICAP) Mean (%)	RSD	Fe_2O_3 (AA) Mean (%)	RSD
UTS-1	0.913	1.96	0.98	1.37	6.9	1.51	6.85	0.94
-2	0.223	5.75	0.23	0	4.53	0.64	4.44	1.46
-3	0.340	2.74	0.37	0	4.63	3.85	4.73	0.66
-4	0.339	6.58	0.37	0	3.64	1.11	3.81	1.53

Standard	Th (ICAP) Mean (%)	RSD	Th (NA) Mean (%)	RSD	U (Fluo) Mean (%)	RSD	U (DNC) Mean (%)	RSD
UTS-1	139	2	134	4.1	59	11	50.9	3.74
-2	179	2.8	168	5.0	56	9.8	53.9	0.82
-3	25	5.8	9.2	4.9	500	0	523.4	1.09
-4	35	10.8	14.2	3.2	1044	1.3	994	0.58

Standard	Ni (ICAP) Mean (%)	RSD	Ni (AA) Mean (%)	RSD	S (Total) Mean (%)	RSD	SO_4 Mean (%)	RSD
UTS-1	45.6	4.31	43	6.4	0.95	1.60	0.94	1.91
-2	25.7	1.22	25	0	2.98	1.22	2.94	1.43
-3	30.1	3.43	25	0	0.21	4.02	0.21	2.67
-4	121.4	0.45	85	0	1.69	1.00	1.68	1.00

Standard	As Mean (%)	RSD
UTS-1	4.5	1.91
-2	20.9	1.43
-3	0.2	2.66
-4	1.7	1.00

TABLE 4

Mean, RSD and Recommended Values for Standards
SY-2 and SY-3 Analyzed by I.C.A.P.

Standard	%Al_2O_3	%CaO	%Fe_2O_3	Ni ppm	Th ppm	%TiO_2%
SY-2						
(n = 4) Mean	12.28	7.97	6.25	15.5	327	0.14
RSD%	1.57	0.57	0.55	3.7%	2.1%	2.7
Recommended Value	12.80	7.98	6.28	10	380	0.14
SY-3						
(n = 4) Mean	11.63	8.19	6.42	16	1017	0.16
RSD%	0.68	1.18	0.70	0	2.63	1.1
Recommended Value	11.80	8.26	6.42	11	990	0.15

TABLE 5

Mean and RSD of A.A. Analyses of Standards SY-2 and SY-3.

Standard		Al_2O_3%	CaO%	Fe_2O_3%	TiO_2%	Ni
SY-2	Mean	13.1	8.61	7.07	0.17	11.25
n = 4	RSD	1.56	1.62	2.05	0	42.6
SY-3	Mean	12.63	9.07	7.29	0.17	15.0
n = 4	RSD	0.79	1.47	0	0	0
Recommended Values						
SY-2		12.12	7.98	6.28	0.14	10
SY-3		11.80	8.26	6.42	0.15	11

TABLE 6

Mean and RSD of Total S, As, U (Fluo), U (DNC) and Th (NA) Analyses of Standards SY-2, SY-3 and MRG-1.

Standard		Th (NA)	U (Fluo)	U (DNC)	As	$S^{=}$
SY-2	Mean	375	310	276	14	-
(n = 4)	RSD	1.53	3.48	0.75	3.3	-
SY-3	Mean	980	731	718	15.8	-
(n = 4)	RSD	0	3.69	0.61	2.5	-
MRG-1	Mean	-	-	-	-	-
(n = 4)	RSD					-
Uncertified GSC Standard mixed with FeS_2	Mean					133
	RSD					16.5%

Recommended Values	Th	U	As
SY-2	380	290	18
SY-3	990	650	20
MRG-1			